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Extended Abstract

## Proteomics characterization of "organic" metal threads - First results and future directions

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As part of a comprehensive project undertaken by the Museum Conservation Institute to better define and characterize all types of metal threads used in textiles, this work specifically focuses on metal threads made with an animal-based organic substrate. This component of metal threads has been overlooked in the past, due to the lack of appropriate analytical methods to study it. The introduction of proteomics to cultural heritage studies has brought a new set of techniques to characterize protein fibers and other protein-based elements of textiles and is thus particularly well suited for the identification of the protein components in complex and multi-layered organic threads.

Organic metal threads were mainly in use between the 11th and 15th century in weaving and were made by gilding an organic material, such as leather, parchment (vellum), animal membrane or paper, and then cutting the gilded material into narrow strips. These strips were used either flat or wound around a fiber core (such as silk, or linen). The introduction of the "metal-coated organic threads" represents a very important achievement in the development of metal threads technology. They were very popular and preferred to the earlier pure gold threads due to the flexibility of the wrapping materials and the reduced price; indeed, the metal coating was applied in one or multiple thin layers on the organic substrate that made up most of the thickness of the thread. These features led to their extensive use in fabric decoration for a variety of textures and visual effects. Up-to-now there has been no systematic classification of organic metal threads and museums have used a variety of terms to refer to them, such as "leather gold", "skin gold", "silvered/gilded goldbeater's skin", etc. In our research, we were able to distinguish membrane threads (from intestines or other tissues) from skin threads (processed animal skin). Our corpus of samples is mainly composed of medieval threads from textiles of Italian, Spanish, and Middle Eastern/Persian origins (Scibè, in progress). Samples from Northern China and Central Asia

complete the corpus for a total of over 70 samples (see acknowledgements for sources of samples). Figure 1 shows two examples of membrane (Italian, 14th C) and skin (Spanish, 13th C) metal wrapped-threads from the Cooper-Hewitt Smithsonian Design Museum.

Starting with samples as small as 1x1 mm, the proteomes of each sample were characterized by nanoLC-tandem mass spectrometry (Thermo Scientific Dionex Ultimate 3000 UHPLC system coupled to a Thermo Scientific LTQ Velos Dual Pressure Linear Ion Trap mass spectrometer). Data files were imported into PEAKS studio 8.5 (Bioinformatics Solutions, Inc.) for searching against protein sequence information available in public databases (Uniprot and NCBI). In addition, because domestic sheep (*Ovis aries*), goat (*Capra hircus*), and cow (*Bos taurus*) were found to be the most common species identified, the identification was validated through a series of distinctive markers from collagen type I and type III chains.

Table 1 shows the proteomics results of the Italian membrane thread 1902-1-257 D compared to a reference substrate of bovine intestinal membrane with silver foil. All proteins identified in the textile sample are shown and separated in collagen and non-collagen proteins. Additional proteins were identified in the reference sample, some of which are shown in Table 1. The proteins identified with the highest protein coverage (%) and number of peptides (#) were the collagen type I chains alpha-1 and alpha-2 (Col1A1 and Col1A2) and collagen type III alpha-1 chain (Col3A1). These three collagen chains were identified as having very similar coverage as the reference sample. Other collagen chains from type IV, V, VI, XI and XIV were identified in the reference membrane, with some of them also identified in the textile sample, but usually with lower coverage. The walls of organs from the digestive and urinary tracts are also made of non-collagenous proteins such as extracellular matrix proteins, cytoskeletal proteins, and smooth muscle proteins, some of which are indicated in Table 1. The smooth muscle proteins, in particular, are contractile proteins found in the muscles that line the internal organs of the body, including the blood vessels, stomach, intestines, urinary bladder, and uterus. As observed in the previous study of a 14th C Italian textile (Popowich, Cleland, and Solazzo, 2018), the analysis of sample 1902-1-257 D showed the presence of smooth muscle proteins of which actin, desmin, and myosin heavy chain 11 were identified with the highest confidence. In the reference membrane, the actin protein was precisely identified as “Actin, gamma-enteric smooth muscle” or ACTG2, characteristic of intestinal muscles, with an 88% coverage and two peptides (WISKPEYDEAGPSIVHR and EEETTALVCDNGSGLCK) unique to the intestinal actin. The less complete identification of actin in 1902-1-257 D, on the other hand, yielded a series of peptides that were also present in actin from skeletal muscles (ACTA1), aortic smooth muscle (ACTA2), cardiac muscle (ACTC1), so that it is not possible to further specify the tissue of origin based on this protein. Desmin is also unspecific as it is found in the intermediate filaments of cardiac muscle, skeletal muscle, and smooth muscle. However, the identification of myosin heavy chain 11, a protein found in smooth muscle only, confirms that an internal organ such as stomach, intestines or bladder is the source of the membrane.

Table 2 shows the proteomics results on the Spanish skin thread 1943-20-1B. The identification of collagen chains in this sample is limited to Col1A1, Col1A2, and Col3A1, typical of skin-based objects. Other collagen and non-collagenous proteins are eliminated during preparation when the skin is turned into parchment, vellum or leather. The skin was best matched to *Capra hircus* (domestic goat) and contained, in addition, the peptide GPSGEPGTAGPPGTPGPQGFLGPPGFLGLPGSR that has been characterized as unique to

goat (Buckley et al. 2010). Skin threads are usually made with an adhesive that can be visualized by UV-reflected microscopy on cross-sections of the threads. The search for a protein-based adhesive revealed the presence of the egg white proteins ovalbumin (most abundant protein in egg white), ovotransferrin, ovoglobulin, and lysozyme from chicken. Threads made with sheep skin and adhesives based on collagen glue, including fish glue, have also been found in threads of different origins, showing a variety of techniques used to make the metal threads.

The information obtained from proteomics has revealed distinct methods of fabrication that will refine our classification of metal-coated organic threads as well as the provenancing of textiles of uncertain origin. Future work will focus on better characterizing the protein adhesives, especially the ones made with fish glue, and understanding the processing method of skin-based threads (parchment vs vellum vs leather).

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FIGURE CAPTIONS

**Figure 1.** a-1902-1-257 D, Italy, 14th century Smithsonian Cooper-Hewitt Design Museum and b-1943-20-1B, Spain, 13th century, Cathedral de Lerida, Spain, Smithsonian Cooper-Hewitt Design Museum. Images acquired by 3D digital light microscopy with HIROX KH-8700, by Cristina Scibè, Museum Conservation Institute, Smithsonian Institution.

**Table 1.** Proteomics results on membrane thread 1902-1-257 D, Italy, 14th century

**Table 2.** Proteomics results on membrane thread 1943-20-1B, Spain, 13th century